PB86-237708

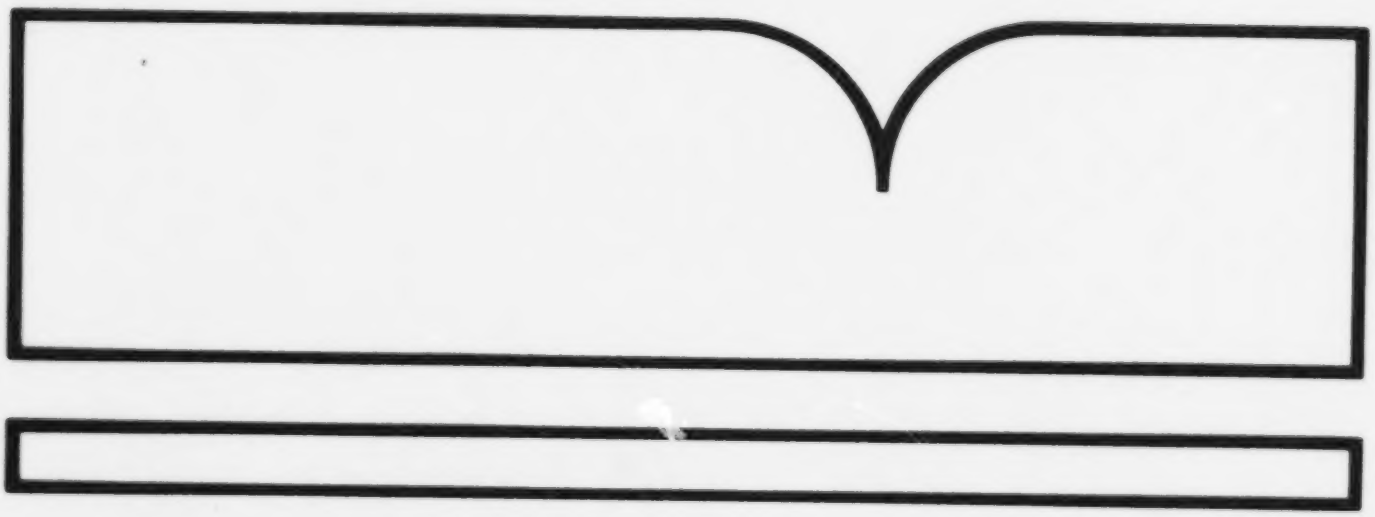
Testing and Evaluation of Permeable Materials for Removing Pollutants from Leachates at Remedial Action Sites

Cincinnati Univ., OH

Prepared for

Environmental Protection Agency, Cincinnati, OH

Aug 86



U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-237708

EPA/600/2-86/074
August 1986

TESTING AND EVALUATION OF PERMEABLE MATERIALS FOR REMOVING POLLUTANTS FROM LEACHATES AT REMEDIAL ACTION SITES

by

James E. Park
Dept. of Civil & Environmental Engineering
University of Cincinnati

68-03-3183
Task 01

Project Officer

Jonathan Herrmann
Land Pollution Control Division
Hazardous Waste Engineering Research Laboratory
Cincinnati, OH 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600.2-86/074	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE TESTING AND EVALUATION OF PERMEABLE MATERIALS FOR REMOVING POLLUTANTS FROM LEACHATES AT REMEDIAL ACTION SITES	5. REPORT DATE August 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) James E. Park	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Civil and Environmental Engineering University of Cincinnati Cincinnati, OH 45221	10. PROGRAM ELEMENT NO. TEJY1A
	11. CONTRACT/GRANT NO. 68-03-3183 Task 01
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory--Cin,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED January 1982 - October 1984
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Jonathan G. Herrmann 513/569-7839

16. ABSTRACT

In order to better understand the potential effectiveness of permeable treatment systems, four readily available, low-cost permeable materials, coal, limestone, fly ash and a soil containing clay - were tested to determine their ability to remove organic pollutants from two simulated hazardous waste leachates. Twelve 20.3 cm x 20.3 cm square columns containing sequencial combinations of the four materials were used to perform the tests. The feed solution of simulated wastes was common to all columns and progressed through the permeable materials by gravity flow. Samples were withdrawn at the interfaces between material layers. The capabilities of the individual materials, as well as, the overall performances of the columns were evaluated with respect to their abilities to retain total organic carbon (TOC) and twelve selected priority pollutants. The results indicated that the most effective ordering of materials was a layer of fly ash, followed by a layer of coal, followed by a layer of limestone.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 54
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract 68-03-3183, Task 01, to the University of Cincinnati. It has been subject to the Agency's peer review, and it has been approved for publication as an EPA document.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local government and the needs of both large and small businesses in handling their wastes responsibily and economically.

This document presents the results of bench-scale testing of the retentive capabilities of layers of low-cost, permeable materials such as coal, limestone, fly ash and soil. The amount of organic pollutants retained as measured by total organic carbon (TOC) was quantified for each material. The most appropriate ordering of the materials in sequential layers was also established.

The intended audience for this document includes those involved in designing remedial action alternatives for treating contaminated groundwater.

Thomas R. Hauser
Director
Hazardous Waste Engineering
Research Laboratory

ABSTRACT

In order to better understand the potential effectiveness of permeable treatment systems, four readily available, low-cost permeable materials - coal, limestone, fly ash and a soil containing clay - were tested to determine their ability to remove organic pollutants from two simulated hazardous waste leachates. Twelve 20.3 cm x 20.3 cm square columns containing sequencial combinations of the four materials were used to perform the tests. The feed solution of simulated wastes was common to all columns and progressed through the permeable materials by gravity flow. Samples were withdrawn at the interfaces between material layers. The capabilities of the individual materials as well as the overall performances of the columns were evaluated with respect to their abilities to retain total organic carbon (TOC) and twelve selected priority pollutants. The results indicated that the most effective ordering of materials was a layer of fly ash, followed by a layer of coal, followed by a layer of limestone.

This report was submitted in fulfillment of Contract 68-03-3183 Task 01 by the University of Cincinnati under the sponsorship of the U.S. Environmental Protection Agency. The report covered a period from January 1982 to October 1984 when the work was completed.

CONTENTS

Foreword iii

Abstract iv

Figures vi

Tables vi

Acknowledgement vii

1. Introduction 1

2. Conclusions and Recommendations 2

3. Literature Review 3

4. Experimental Procedures 9
   - Experimental Design 9
   - Materials and Feeds 11
   - Analytical Methods 15
   - Batch and Elution Test Procedures 15
   - Calculation of Retention 16

5. Results and Discussion 19
   - Breakthrough Curves, Retention and Elution 19
   - Batch Tests 28
   - Movement of Priority Pollutants 31
   - Overall Column Performance and Ordering of Materials 33

6. Conceptual Design Examples 34
   - Assumptions 34
   - Conceptual Design 1 35
   - Conceptual Design 2 36
   - Conceptual Design 3 39

References 43

FIGURES

NUMBER		PAGE
1	Bench Scale Apparatus	9
2	Materials Ordering	10
3	Particle Size Distribution	13
4	Idealized Breakthrough Curves for a 3-Layer Column System	17
5	Breakthrough Curves for Columns 1 and 2, Runs 1 and 2	20
6	Breakthrough Curves for Columns 3 and 4, Runs 1 and 2	21
7	Breakthrough Curves for Columns 5 and 6, Runs 1 and 2	22
8	Breakthrough Curves for Columns 7 and 8, Runs 1 and 2	23
9	Breakthrough Curves for Columns 9 and 10, Runs 1 and 2	24
10	Breakthrough Curves for Columns 11 and 12, Runs 1 and 2	25
11	Run #1 Retention Results	29
12	Run #2 Retention Results	30
13	Conceptual Design 1: Boundary Barrier	37
14	Conceptual Design 2 & 3: Collection System	38
15	Flushable Treatment Trench	40
16	Modular Treatment Trench	42

TABLES

1	Composition of Coal and Fly Ash	12
2	Properties of Materials	13
3	Priority Pollutants in Feed #2	14
4	Run #1 Column Performance	26
5	Run #2 Column Performance	27
6	Batch Test Results	28
7	Run #2 Priority Pollutant G.C. Analysis	32

ACKNOWLEDGEMENTS

This work was performed at the U.S. EPA's Test and Evaluation Facility under the auspices of the University of Cincinnati's Contract No. 68-03-3183, Task 01. Ms Yu-Lin Liu provided considerable help in performing the experiments. Mr. Richard J. Lesiecki provided assistance in the preparation of this report. The Technical Project Monitor was Jonathan G. Herrmann, of the Land Pollution Control Division, who furnished providential guidance.

SECTION 1

INTRODUCTION

The selection of remedial action alternatives at a hazardous waste site depends on many site-specific characteristics. Given the possible variations in hydrogeology, soils and wastes it would be desirable to have a number of alternatives from which to choose. The goal of many remedial action alternatives is to enclose a site by constructing impermeable barriers, cutting the site off from both surface water and groundwater flow. While this type of action may be successful in diverting or stopping the movement of contaminants, the levels of contamination are not mitigated. In fact, the concentrations against an impermeable barrier may even jeopardize its integrity.

The use of permeable, sorptive materials in a treatment barrier (or system) is an option that does not simply halt contaminant movement. A permeable treatment system can not only remove contaminants from groundwater, but it also allows the treated groundwater to flow from the site. The physical and chemical processes that remove contaminants from polluted goundwater include precipitation, physical and chemical adsorption, ion exchange and filtration. The term retention is used to describe the total effect of all the mechanisms which retard the movement of contaminants.

Materials such as coal, limestone, fly ash, and soils containing clay have the retentive capabilities and low costs that make them useful in permeable treatment systems. The manner in which these materials are used in a permeable treatment system depends upon the particular site characteristics. Alternatives include vertical walls intercepting groundwater, horizontal beds used to treat pumped leachate and provide a source of recharge, or in-ground modular systems which can be replaced after the materials have reached their retentive capacities.

In order to test the permeable treatment system concept, simulated hazardous waste leachates were contacted with various combinations of sequentially ordered layers of coal, limestone, fly ash and a soil containing clay. The results provided a qualitative indication of the systems' efficacy as well as design information. This information would be essential prior to the design and installation of a field application of a permeable treatment system. Several conceptual designs for permeable treament systems as remedial action alternatives were developed, using the experimental data.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

1. The results of this project show that low-cost permeable materials such as coal, limestone, fly ash, and soil containing clay can retain contaminants from simulated hazardous waste leachates. Using total organic carbon (TOC) as an indication of the presence of organic contaminants, coal retained 498-813 mg TOC/kg, fly ash 286-323 mg TOC/kg, limestone 0-98 mg TOC/kg, and a soil containing clay 348-522 mg TOC/kg.

2. The priority pollutants spiked into the feed of Run #2 exhibited various relative mobilities. Dichlorophenol, phenanthrene, pentachlorophenol, fluoranthene and pyrene had limited mobility, while Bis (2-ethylhexyl) phthalate, Di-N-Butyl phthalate, phenol, 1,2 dichlorobenzene, isophorene, napthalene and ethylbenzene moved through the columns at the same rates as measured by the TOC data.

3. The most effective ordering sequence considering the permeable materials and the simulated hazardous waste leachate used was a layer of fly ash, followed by a layer of coal, followed by a layer of limestone.

4. The experiments helped establish the efficacy of the concept of using permeable materials, but the test apparatus is inefficient for rigorous testing. The second run lasted 47 days and consumed almost 700 L of feed.

Given the results and the observations made during this project, the following recommendations are offered.

1. A scaled-down, bench test system should be developed that would provide results faster than the 30-47 days required for the experiments performed for this project. The results should be verified by comparison with the previously performed work.

2. Various solutions for flushing contaminants from the retentive materials, should be tested followed by an assessment of the flushed permeable materials' retentive capacities. This would provide information on the utility of flushable permeable treatment systems.

3. The design and testing procedures for permeable materials should be demonstrated by installing and evaluating a pilot-scale or larger permeable treatment system. Installation at a remedial action site should be considered.

SECTION 3

LITERATURE REVIEW

The concept of using permeable materials that can retain constituents from a contaminated liquid is not new. Except for the use of activated carbon though, this concept has not been applied at field-scale for remedial action at an uncontrolled hazardous waste site. Pertinent laboratory-scale work has however, been performed on specific materials and feed solutions. A small number of pilot-scale projects have also been completed.

The materials likely to be used in a permeable treatment system can be divided into three categories: 1) synthetic and industrial products, 2) natural materials, and 3) waste materials. Included in the first category are activated carbon and alumina, commercial sorbents and manufactured zeolites. These materials have been used extensively in treating wastewaters and their sorptive capabilities are well understood. The common problem associated with these materials with respect to a remedial action activity is their high cost. Since the purpose of the project was to evaluate low-cost materials, synthetic and industrial products were not addressed, but could conceivably be useful in a permeable treatment system.

The second category includes materials such as coal, limestone, soil containing clay and natural zeolites of which greensands are an example. These naturally occuring materials are generally available at low cost depending on geographical location. The third category includes waste materials such as fly ash, bottom ash and lime-sludge from flue-gas desulfurization. These would be available depending on the proximity to a coal-fired power plant.

Coal

Coal is a generic term for a substance that is a chemically and physically-complex mixture of organic compounds and polymers, as well as crystalline minerals. The mineral matter in a coal can vary from 5 to 35%, which can include up to 50% clay minerals and lesser percentages of carbonates, sulfides and silica. Coal also can contain significant amounts of trace elements. As, B, Be, Co, Cd, Pb, Mo, Ni, Sn and Zn are commonly found in the mg/kg range.

Coal's ability to retain hazardous waste components is two-fold; the organic portion of the coal has sorptive sites in its pores similar to those found in activated carbon, while coal's mineral portion usually contains a high percentage of clay, which can sorb both organics and metals. Coal's

ability to retain inorganics has been documented by Wang (1980) and Walters and Niemczyk (1982). The latter authors confirm that most (95%) of the sorption of inorganics is by the mineral portion of the coal and should be considered as ion exchange. Coal's retention of metals in column studies to greater extents than in batch tests has been reported by Wang (1980) and Park (1983). Coal's retentive capacity is influenced by pH, coal rank and composition, and the concentration of solutes.

Coal itself is a predominantly organic material. Unlike activated carbon, there has not been a great body of literature generated concerning its sorptive capacities. Two papers: Wang (1980) and Humenic, et al (1982) deal with batch tests examining the sorption of certain organic compounds by coal.

For the compounds investigated in these experiments (phenol, p-cresol, 2,6-dimethyl phenol, a-naphthol, benzene, toluene, xylene, naphthalene, aniline, quinoline and indanol) at concentrations mostly below 10 ppm, the adsorption coefficients compare favorably with the values for activated carbon (Dobbs and Cohen, 1980) and in some cases exceeded them. Despite this evidence, there is no reason to believe that coal will generally retain organics better, or even nearly as well as activated carbon.

Limestone

Limestone is a naturally-occurring rock that is composed of varying proportions of calcite ($CaCO_3$), arragonite ($CaCO_3$) and dolomite ($CaMg\ [CO_3]_2$). It is alkaline and usually has a pH between 8 and 9 (Boynton, 1980). Agricultural limestone, usually crushed to a fine, granular form has been used extensively to raise the pH of soils.

Fuller, et al, (1976b) studied the batch adsorption of many trace elements by limestone and suggested that the anion-forming elements are retained as well as some of the cation-forming elements but seemed to be held less tightly and may desorb with continued leaching. The elements investigated that had retentions in the range of 100-1000 mg/kg limestone included: Ni, Zn, Cr, Cd, As, Be, Hg, Se and V; Pb, Cu and Al all exhibited retentions much greater than 1000 mg/kg. Following column studies to determine the effect of a 1-cm layer of limestone on various soils' retention of the trace elements, Cd and Ni were found to have been better retained, while little effect was noticed for Cr, As, Se and V.

Artiole and Fuller (1979, 1980) in column experiments, investigated layered limestone's ability to increase soils' retention of Be, Cd, Fe, Ni and Zn in leachate. The authors stated that crushed agricultural limestone delays the rate of migration of the five metals (Be, Cd, Ni, Fe and Zn) through the soil material by as many as 5 to 10 pore volumes displacements. The major mechanism responsible for the retention of these metals was precipitation as carbonates of Be, Fe and Ni; Cd and Zn were removed primarily by ion exchange/adsorption, with precipitation playing a secondary role. The authors note a difficulty in separating the retention by the limestone alone from that which takes place in the soil.

Limestone itself appears to exhibit some retention in batch tests but this is not substantiated by the column studies. Its essential usefulness is in raising the pH of the leachate in order to facilitate precipitation of cations, not in retaining them on its surface.

Although the experimental work concerning limestone's ability to remove organic constituents is sparse, it would be reasonable to say that it is not an effective sorbent. For the 11 soils with layers of limestone above them, studied by Fuller, et al, (1981) limestone was ineffective in attenuating an initial TOC of 7000 mg/L. In most cases, the soil/limestone combinations used were saturated with TOC within three to four pore volumes of flow through the columns, or less.

Limestone's limited ability to retain organics is accompanied by two negative, though probably less significant, effects. The first, as noted by Artiole and Fuller (1979), is that organic material may coat the surface of the limestone, reducing its ability to contribute Ca to solution and raise the pH. This reduces its effectiveness in precipitating metals and thus its useful life. The second detrimental effect is the increased mobility of metals in the presence of organic matter. This has been noted in the experiments mentioned in this section, as well as in Artiole and Fuller (1980). Since limestone appears to provide little retention of organics, metals complexed with the organics would not be retained and would migrate without precipitating.

Fly Ash

Roy, et al (1981) provides a comprehensive review of the fly ash literature and is the source of the uncited information used in this discussion. Fly ash is a by-product of industrial and utility coal-fired boilers. It is usually a combination of mechanical and/or physical (e.g. electrostatic precipitators) collection of the particles in the stack gas and may also include the slag or bottom ash that falls out in the bottom of the furnace.

Generally, the material has a texture similar to that of a silty loam but may vary from a fine powder to a fine granular consistency. Its specific gravity usually falls within a range of 2.1 to 2.6 g/cm^3.

As a mineral, fly ash can be characterized as an amorphous ferroaluminosilicate. Many of the trace elements found in fly ash volatilize, then condense on the particle surface in the stack. These trace elements, as well as some of the more dominant elements such as calcium, are thought to be only slightly bonded to the surfaces and are susceptible to removal by dissolution, for example. The trace element composition of fly ash varies with the coal.

Because the type and composition of coal varies a great deal, the chemistry of fly ash in water can really only be generalized. Coals that have higher contents of Ca and Mg, and a lower content of sulfur, that are usually considered, "Western" coals, will produce a fly ash with a basic pH. "Eastern" or "Midwestern" coals, higher in sulfur and iron, on the other hand,

will usually produce a more acidic fly ash (Elseewi, et al, 1980). Theis and Wirth (1977) found direct association between Fe oxides and acidity and the presence of Ca or free lime and basicity.

Generally, the active sites of sorption on fly ash particles are the oxides of iron, manganese, and aluminum, the effectiveness of which appears to depend on maintaining oxidizing conditions (Theis and Richter, 1979). Chan, et al (1978, 1980) and Sheih (1979) reported good removals of Ca, Mg, Cu, F and CN from industrial sludge leachate. Their work included batch, column and pilot-scale beds. In the same experiments, the authors determined fly ash retained organics, as measured by TOC, between 45 mg/g and 1468 mg/g depending on the concentration of the leachates. This compared well with the activated carbon they tested with the same leachate. These retentions are rather high and may reflect a particular affinity for fly ash by these unnamed organics.

Soil Containing Clay

The clay component of the soil at or near a site can effectively sorb both organic and inorganic contaminants. A good correlation between a soil's clay content and its ability to sorb metals has been noted by Farquhar (1977) and Griffin, et al. (1977). Two groups of studies, by Griffin, et al. (1976a, b, c, 1977) and by Fuller, et al. (1976a, b, 1979, 1980), Korte, et al. (1975, 1976a, 1976b) and Alesii (1976), have addressed the movement of various metals through different soils with different clay contents.

Griffin et al found that of the three basic types of clay minerals, montmorillonite retained metals better than illite or kaolinite. For the metals tested, those that were considered to be highly attenuated were: Pb, Zn, Cd and Hg. Precipitation was believed to be the mechanism. Those showing moderate attenuation were: Fe, Si, K, NH_4 and Mg, possibly attributable to ion exchange; Na and Cl showed little attenuation, while Ca, Mn and B were not retained at all.

Fuller et al. (1976a, b, 1979, 1980, 1981) studied the movement of inorganics through 11 representative soils. They found that the percent of clay in the soil was the most useful means of predicting a soil's ability to retain a particular element. They also found a good correlation between retention of anions and the amount of free Fe oxides.

The interactions of inorganics and soils as described by Fuller et al., may be summarized:

- The amount of clay in a soil may be the most useful indicator of its ability to sorb inorganics, especially cations.
- Cations are removed from solution by precipitation or ion exchange on the clay mineral surface.
- Anions such as As, Se, C and CN will be mobile in alkaline soils. They can be sorbed in anion exchange reactions or by the hydrous oxides of Fe, Mn or Al, which are present in most soils.

Organics interact with soils with more complexity than do inorganics. A theoretical understanding of the sorption of organic molecules by clay minerals was outlined by Grim (1968): organics are held by both Van der Vaals and columbic forces, and larger molecules cannot replace smaller molecules on sorptive sites. Chain length and methane activity were also noted as affecting sorption.

Dragun and Helling (1981, 1982) state that lipophillic attraction to soil organic matter, electric charge, and the amount and type of clay affect the retention of organics. They also suggest a correlation between a compound's water solubility and its mobility in soil. The surfaces of clay minerals are hydrophillic, so they do not sorb molecules with low water solubility. Furthermore, compounds that may undergo free radical oxidation, such as benzene, benzidine, naphthalene and phenol, may be more likely retained. Compounds that do not undergo this reaction include dioxin, hexachlorobenzene (HCB), hexachlorocyclopentadiene (C-56), kepone, mirex, PCB and PBB's.

Work on sorption of individual compounds has been done by Davidson (1976, 1980), Griffin and Chou (1980), Chou et al. (1980, 1981).

Other Materials

Other materials that may prove useful in permeable treatment systems include greensands, limewastes and synthetic and industrial products.

Greensands

Greensands are a type of soil common to the Eastern seaboard. They contain large portions of glauconite, a hydrous alumino-silicate rich in ferric iron, which is thought to be the dominant sorptive site. Spoljaric and Crawford (1979a,b) investigated the sorption of metals commonly found in industrial waste, by greensands. As, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Au and Zn were all sorbed. Some elution with tap and distilled water was noted. The authors provided no evidence of greensand's ability to sorb the organic present in the industrial wastes tested.

Limewastes

Similar to limestone, limewaste sludges from flue gas cleaning operations are available and will be so in increasing quantities as scrubbing at coal-fired power plants becomes more common. Little work has been done with this material. It should contain sulfate and sulfite calcium compounds instead of the carbonate found in limestone. The fly ash that may also be present may afford some sorptive capacity.

Synthetic and Industrial Products

There are many commercially-available materials, for the most part synthetic, that are widely used by industry for sorbing metals and organics. Included in this category would be natural and synthetic zeolites, ion exchange resins, and a host of proprietary sorbents developed for specific types of chemicals.

Ion exchange resins, which have been used since the 1940's, have higher sorptive capacities per unit weight than most natural materials. Manufactured zeolites have exchange characteristics similar to ion exchange resins, but usually consist of aluminosilicate in a tetrahedral framework having loosely-held H_2O molecules permitting reversible hydration. These materials have been used in water softening for many years.

The sorption of metals from solution by synthetic materials is fairly well understood. One example is provided by Malone and Karm (1982). They immobilized diamines on silica gel and successfully removed Cr, Cu, Cd, Ni, Pb and Zn from an electroplating waste stream. By contrast, the sorption of organics by synthetic materials is indeed a complex subject. A report by Herrick, et al, (1982) presents information on the compatibility of certain commercial sorbents with chemicals most commonly found in hazardous waste spills; by sheer numbers, most sorbents are organic. Some sorptive capacities are included, but by and large, the specifics of sorptive behavior with hazardous waste are unknown.

The one thing most synthetic and industrial products have in common is that they are generally more expensive than the other permeable materials discussed in this report. As a group, though, they may be considered to have higher sorptive capacities per unit weight than the low cost, natural and waste materials and, if they are compatible with the contaminants, may prove useful as additives to a permeable treatment system.

SECTION 4

EXPERIMENTAL PROCEDURES

EXPERIMENTAL DESIGN

The literature review indicated that no single material has the ability to retain all the possible combinations of contaminants commonly found in hazardous waste leachate. This leads to a treatment system comprised of multiple layers of different permeable materials. The orderings of these materials, their retentive capabilities, and the effects of any interactions between layers of materials all require evaluation. These were the objectives of the experiments conducted.

A schematic of the test apparatus is shown in Figure 1. Two connected units, each containing six 20.3 cm x 20.3 cm square columns were used for a total of twelve columns. All columns were packed by hand to a depth of 36 cm. The feed solution flowed over the column separations so that each column received the same feed. Each columns's flow was controlled by a valve which provided steady drips into an effluent collection vessel. Porous stones connected by tubing to the column's exterior were placed at the interfaces between materials to provide sampling access. These interfacial sampling ports permitted monitoring of the changes in pollutant concentration during leachate passage through each layer.

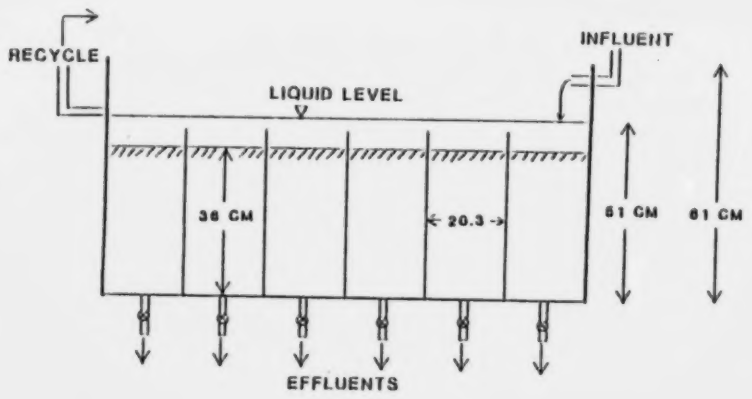


Figure 1. Bench Scale Apparatus

The orderings of the four permeable materials in the 12 columns are shown in Figure 2. These orderings were used in both experimental runs. The thinnest layers were 6 cm, the layers of intermediate thickness were 10 cm and the thickest layers were 20 cm. The top layers of coal and fly ash were duplicated in pairs of columns: coal in 3, 4 and 7, 8, and fly ash in 1, 2 and 5, 6. The top layer of soil was duplicated in 9 and 10. Columns 11 and 12 were used to test 36 cm layers of fly ash and coal respectively, which were expected to exhibit the best retention of the four materials. The pairings of the top materials allowed the evaluation of contact with unaltered feed solutions.

Based on the literature, limestone was expected to have minimal retentive capacity for organics. It was though, expected to affect precipitation my means of raising the pH of the feed.

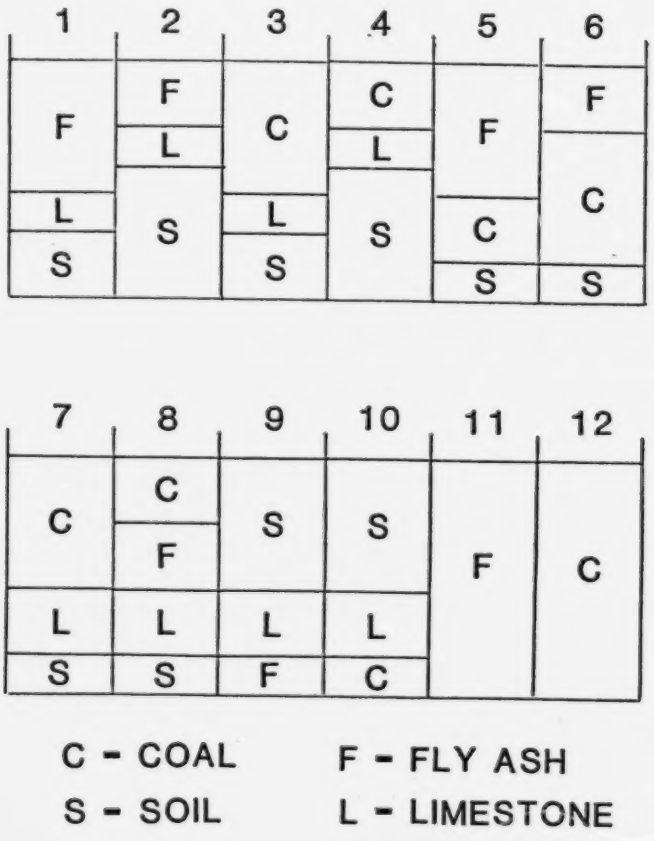


Figure 2. Materials Ordering

MATERIALS AND FEEDS

Permeable Materials

The rationale for choosing the permeable materials was straight forward: at a remedial action site, most permeable materials would be procured from local sources; therefore, the four materials chosen were obtained from Cincinnati-area sources.

The limestone was obtained from a commercial source near the Little Miami River in Southwestern Ohio. It is known as "#9" and consists of small chips that pass a #9 sieve. For the second run, these chips were mixed with crushed agricultural limestone in a 1:1 ratio. The agricultural limestone was purchased from a local retailer and was the texture and size of beach sand.

The fly ash was obtained from the Miami Fort Power Plant at North Bend, Ohio. Its mineral characteristics are presented in Table 1. It was grey-brown in color. The particle-size distribution is presented in Figure 3. The material had a basic pH (~10.0) when allowed to equilibrate in deionized water.

The coal was purchased from a local supplier. It is referred to as "bit-slack" and was mined near Stinson, Kentucky. Its proximate and ultimate analyses, as presented in Table 1, indicate that it is sub-bituminous. Its particle size distribution is shown in Figure 3. This coal, equilibrated with deionized water, is acidic (pH ~ 3.2).

The soil was taken from a recently excavated site in Northerm Hamilton County, Ohio. It contains a significant portion of clay-sized particles, as seen in Figure 3.

The in-place densities, permeabilities and pH's of the materials are presented in Table 2. The densities were calculated from the dry weights of the materials as placed in the columns. Standard compaction permeameter tests were run on all materials except limestone which had large sized particles. pH was determined by placing 50 g of a materials in 100 ml of deionized water.

Simulated Hazardous Waste Leachates

Since inorgranics have been studied much more in past research than organics, the emphasis of these experiments was on the retention of organic contaminants.

TABLE 1. COMPOSITION OF COAL AND FLY ASH

COAL

Proximate Analysis *	As Rec'd %	Ultimate Analysis +	Dry Basis
% Moisture	3.60	H	4.33
Volatile	30.48	N	1.20
Fixed Carbon	52.89	O	13.67
Ash	13.02	C	66.32
Sulfur	.81	S	.84
		ASH	13.51

Chemical Analysis (of ash) †

	Coal Ash	Fly Ash
Silica Dioxide	63.01	53.78
Ferric Oxide	6.66	16.10
Aluminum Oxide	25.85	24.74
Titanium Oxide	2.22	.54
Calcium Oxide	.04	2.14
Magnesium Oxide	.10	.25
Sulfur Trioxide	.40	.43
Potassium Trioxide	1.13	.64
Phosphorus Pentoxide	.50	.53
Sodium Oxide	.09	.35

* The proximate analysis accounts for only the five components listed, but is useful in determining the coals's rank.
+ The ultimate analysis determines the elemental portions present as well as the ash component.
† The chemical analysis is a determination of the minerals present in the ash from the ultimate analysis. The second column here is the fly ash as received from the power plant.

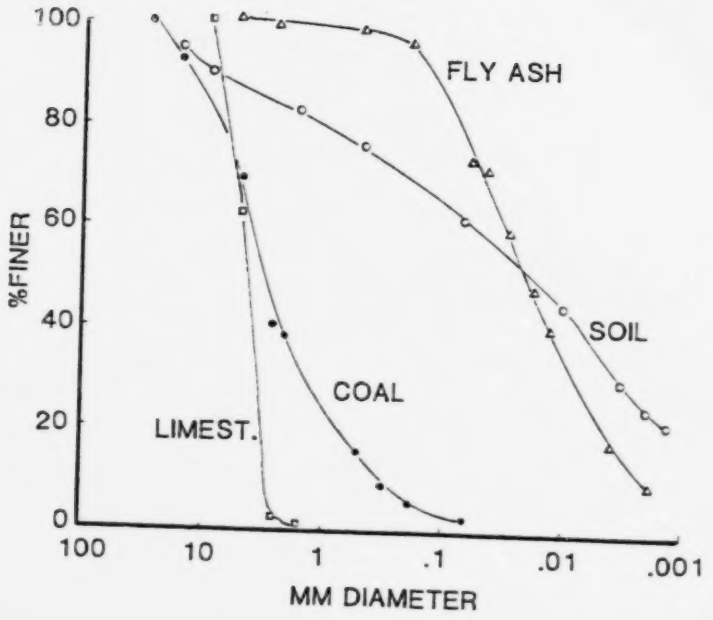


Figure 3. Particle Size Distribution

TABLE 2. PROPERTIES OF MATERIALS

	Density in Column g/cm^3	pH *	Permeability (cm/sec)
Coal	.905	2.5	$1.8 - 6.6 \times 10^{-4}$
Fly Ash	1.30	10.3	$5.3 - 7.0 \times 10^{-5}$
Limestone	1.85	7.7	- †
Soil	1.39	7.7	$1.7 \times 10^{-4} - 3.5 \times 10^{-5}$

* 50 g of material in 100 ml of deionzied water.
† The limestone was granular, so no permeability tests were performed.

The simulated hazardous waste leachate used in the first run was obtained from 20 experimental municipal landfill lysimeters. The leachate was the result of municipal solid waste co-disposed with various sludges. Although analytical results were not available, the organic portion of the leachate was believed to be made up mostly of fatty acids, while iron was the dominant inorganic component. Phenol and dichlorobenzene were added to this leachate at concentrations of 400 mg/l and 80 mg/l respectively. The initial TOC of the simulated feed was 2500 mg/l. Over the length of the run it dropped to 400 mg/l due to volatilization and decomposition. The flow weighted average TOC values for the 12 columns in Run #1 ranged from 1115 mg/l to 1596 mg/l. The total TOC applied to each column was determined by summing daily flows times that day's TOC concentration.

The feed for the second run was prepared daily in 15 L batches. It was comprised of 0.1N$CaSO_4$, 850 mg/l KHP (postassium hydrogen phthalate), 100 mg/l toluene and the priority pollutants in Table 3, at the concentrations listed.

TABLE 3. PRIORITY POLLUTANTS IN FEED #2

	Actual Conc. (μg/l)
Bis(2-ethylhexyl)Phthalate	163
Di-N-Butyl Phthalate	128
1,4 Dichlorobenzene	192
2,4 Dichlorophenol	109
Ethylbenzene	261
Fluoranthene	129
Isophorone	120
Pentachlorophenol *	136
Phenanthrene *	
Phenol	115
Pyrene	135
Naphthalene	137

* These two compounds could not be distinguished in the analytical procedure.

ANALYTICAL METHODS

Total Organic Carbon (TOC)

Daily effluent and interfacial samples were analyzed for their total organic carbon content. All samples were analyzed within 24 hours, so sample preservation was unnecessary. The instrument used was an Astro Resources Model 1850 TOC-TC Analyzer equipped with an autosampler. It utilized a strong oxidizing agent (sodium persulfate) in the presence of UV light to convert all organics to CO_2, which is then measured by an infrared analyzer. All samples were run in triplicate and were automatically acidified and sparged prior to injection into the instrument in order to remove inorganic carbonates. EPA Method 415.1 was followed and quality control samples obtained from USEPA's Environmental Monitoring and Support Lab were run daily.

Gas Chromatographic Analysis

Run #2 effluent samples from all columns were collected and composited over 5-day periods. These were refrigerated until the analysis could be performed. Gas chromatographic analysis following EPA Method 602 was performed on the composites to determine the concentrations of the compounds listed in Table 3. Three duplicates were analyzed for each 5-day batch of composites. The analyses were performed by USEPA laboratory personnel.

BATCH AND ELUTION TEST PROCEDURES

Batch Leaching Tests on Materials

In order to determine the amount of organic carbon present in the unaltered materials, 40 g of each individual material was placed in a sealed container with 100 ml of deionized H_2O. Following 24 hours of hourly aggitation the liquid was filitered with .45 μ filters and analyzed for TOC.

Batch Test Procedures

As a commparison with the column studies, batch tests using simulated hazardous waste leachates were conducted. For the first run, two concentrations of phenol (100 mg/l and 200 mg/l) were contacted with 120 g of each material. 300 ml of liquid was used to provide the same solid/liquid ratio as in the leaching tests. After 24 hours of hourly agitation, followed by .45 μ filtration, the liquid was analyzed for TOC.

The batch tests for Run #2 made use of that run's simulated hazardous waste leachate. Because there was only one feed concentration, the amount of the material was varied. Twenty, 30 and 40 grams of coal, fly ash and soil were contacted with 300 ml of the Run #2 leachate. These samples were agitated, filtered and analyzed for TOC.

Elution Test Procedure

Elution tests were performed on the leachate-saturated materials from Run #2. This test showed how much of the total organic carbon retained by the materials could be flushed from them. A 50 g sample representative of each layer of material in Run #2 was placed in a sealed container with 300 ml of .1N$CaSO_4$ in tap water. This solution simulated a groundwater flushing through the materials. After 24 hours of periodic agitation, the supernatant was analyzed for TOC.

The moisture content of the samples was determined by drying at 30°C. The amount of TOC eluted from each sample was then calculated on a dry weight basis.

CALCULATION OF RETENTION

As the sumulated hazardous waste leachate passes through layers of permeable materials, constituents of the leachate remain on the materials, essentially moving from the liquid leachate to the solid material. The various mechanisms that describe this movement include adsorption, ion-exchange, precipitation, filtering and chemical bonding. For the purposes of this research no differentiation between mechanisms was attempted. The aggregate effect of all mechanisms with respect to a constituent can be termed retention. The constituent measured in both experimental runs was total organic carbon (TOC); the calculations then determine the amount of TOC retained by each layer of material in every column.

Figure 4. shows the idealized results of a column system containing three layers of permeable materials. The three curves represent the changing values of TOC concentration as measured at two sample ports located at interfaces between layers of materials and as measured in the column effluent. These values have been normalized with respect to concentration and flow volume according to the following equations.

$$C_N = \frac{C}{C_{Max}} \quad \text{and} \quad Q_N = \frac{Q}{Q_{Total}}$$

where,

C_N = The normalized TOC concentration value corresponding to a given normalized, cummulative flow value, Q_N

C = The TOC concentration (mg/l) of a given sample, corresponding to a given cummulative flow Q(l).

C_{Max} = The TOC concentration (mg/l) of the leachate feed, or the highest concentration found in the column.

Q_N = The normalized, cummulative flow corresponding to a given normalized concentration C_N.

Q = The cummulative flow (l) corresponding to a given sample concentration in a given column.

Q_{Total} = The total cummulative flow (l) through a given column over the length of the run.

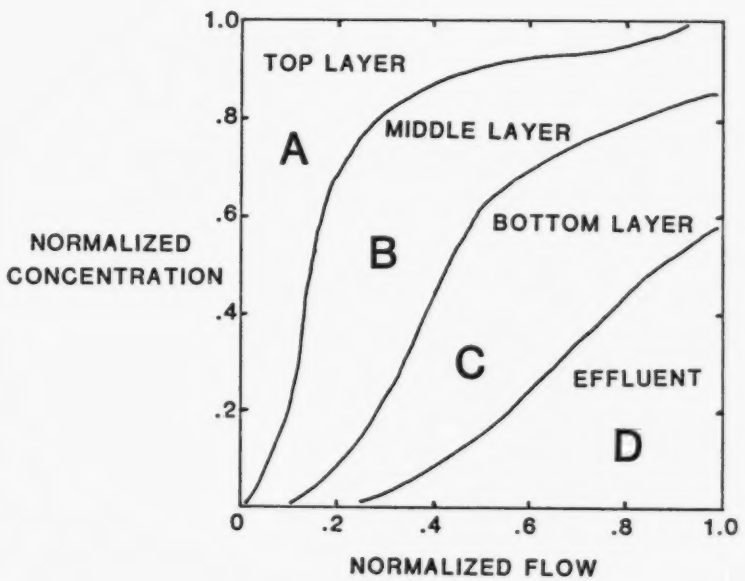


Figure 4. Idealized breakthrough Curves for 3-Layer Column System

The idealized column breakthrough curves shown in Figure 4 are plots of C_N vs Q_N for the two interfacial sample ports and the column effluent. These three curves divide the graph into four areas, labled A, B, C and D. The total area of the graph is equal to the total input of TOC, since the values have been normalized, this area also equals 1.0. By determining the areas labeled A, B, C and D, the respective proportions of total input TOC retained by each corresponding layer can be found.

The areas under each of the curves generated for the 12 columns, in each of the two experimental runs, were determined by summing the trapezoidal areas between successive pairs of data points. By calculating the area under the curve for the column effluent, the area labeled 'D' in Figure 4 can be determined. This is the amount of TOC (mg) not retained by any of the layers in the column. The total TOC input is known, (feed concentration times total flow) so the difference is the amount of TOC (mg) retained by the column as a whole. This total is then divided among the three layers according to their respective proportions of area. The result is an amount of TOC (mg) retained by each layer of a given column. Knowing the dry weight of each material as placed in a column, the amount of TOC retained can be determined as milligrams per kilogram of material.

SECTION 5

RESULTS AND DISCUSSION

BREAKTHROUGH CURVES, RETENTION AND ELUTION

The data from the two experimental runs are presented as breakthrough curves for the sample ports and effluent of each column. These are found in Figures 4 through 27. For all Run #1 curves the concentration data was normalized by dividing by the maximum concentration found in each column, which ranged from 2000-2500 mg/l TOC. All concentration data from Run #2 was divided by 421 -(mg/l TOC) which was the average leachate feed concentration. The total flows for each column, used to normalize the cumulative flow volumes are found in Tables 4 and 5.

Because the same materials in the same orders were used in both experimental runs, similarities in the breakthrough curves for replicated columns would be expected. Many column pairs for the two runs have breakthrough curves with similar slopes and proportional spacings between curves. The main difference between the two runs was the much higher TOC concentration of the Run #1 simulated hazardous waste leachate. An artifact of this first run, the drop in concentration near the end of the run, was attributable to the drop in TOC concentration of the feed leachate which was discussed in Section 4.

The retentive capacity results for the individual layers of permeable materials are shown in Figures 11 and 12. These values were calculated from the breakthrough data as described in Section 4. Coal retained on average for both runs more TOC than the other materials. The soil retained less than the coal, and like the coal, retained more TOC in Run #1 than Run #2. Since both of these materials retained more TOC when contacted with a higher concentration, their retentive capacities should be at least in part due to adsorption, this reaction being concentration dependent. Fly ash on the other hand retained on average slightly more TOC in Run #2 than in Run #1 despite the higher concentration. This would indicate that adsorption accounted for very little of the fly ash's retentive capacity. Limestone retained very little of the TOC in either run.

As a way of checking on how much TOC was retained by each material and how strongly it was held, elution tests as described in Section 4 were run on samples taken from the concentration-saturated material from the Run #2 columns. These values are found in parentheses in Figure 12. In the case of fly ash, all the retained TOC was eluted. This supports the contention that fly ash's retentive capacity was not due to adsorption as the TOC would be

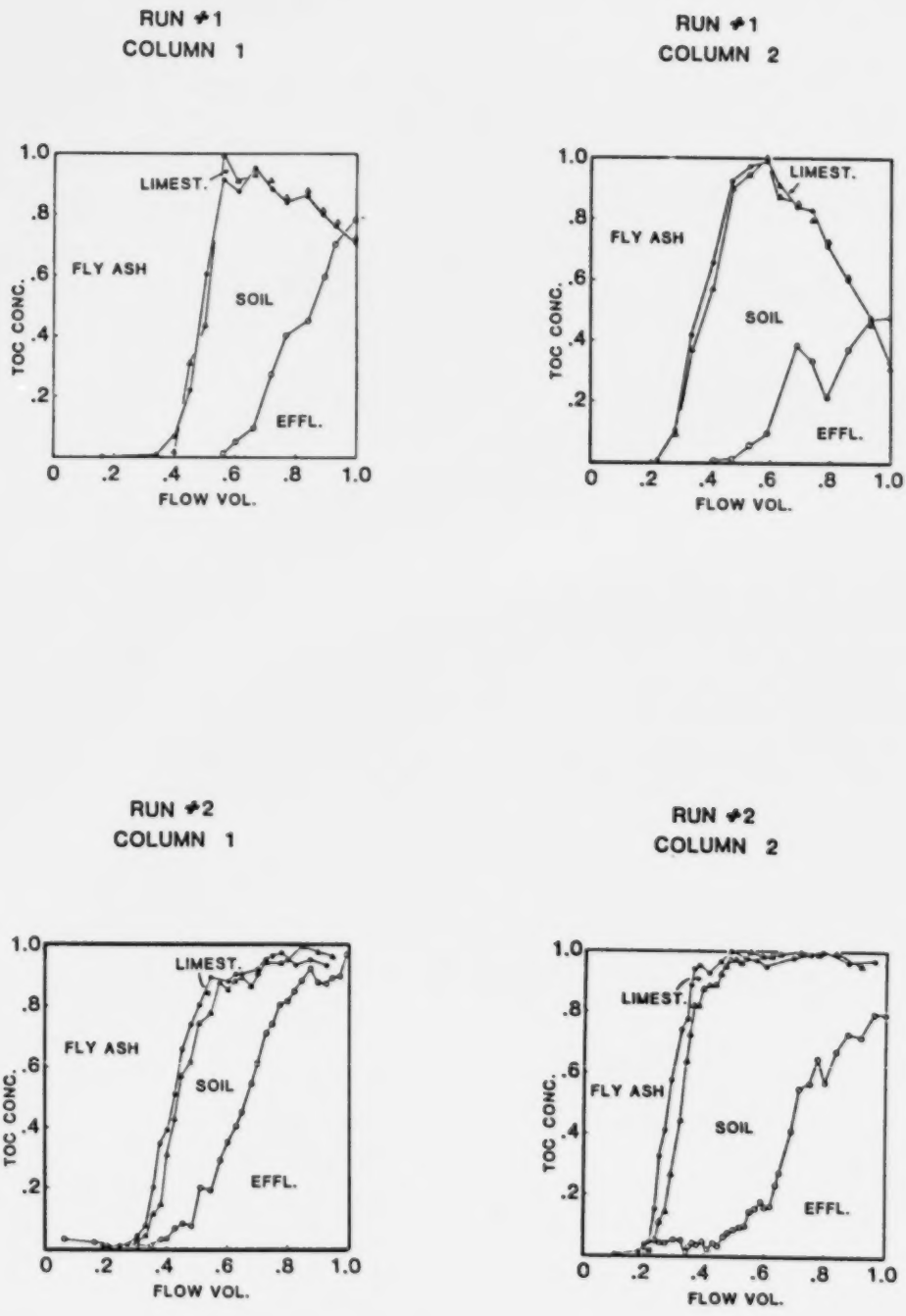
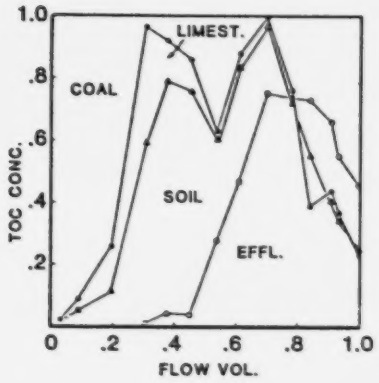
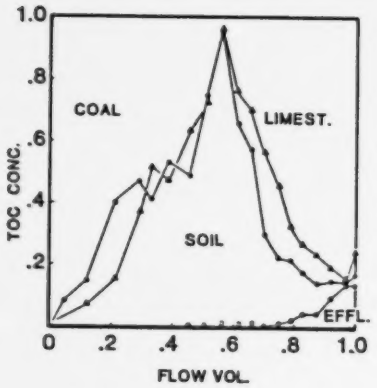


Figure 5. Breakthrough Curves for Columns 1 and 2, Runs 1 and 2

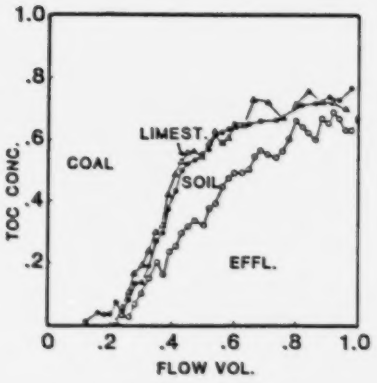
RUN #1
COLUMN 3



RUN #1
COLUMN 4



RUN #2
COLUMN 3



RUN #2
COLUMN 4

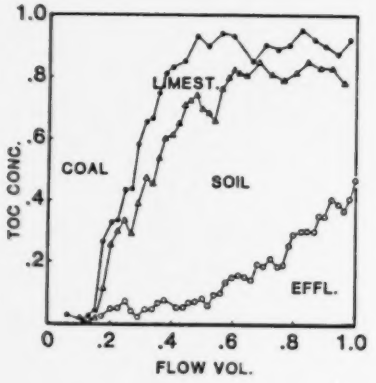
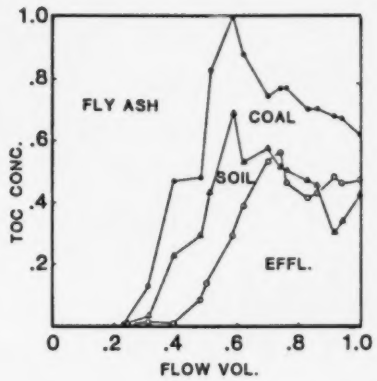
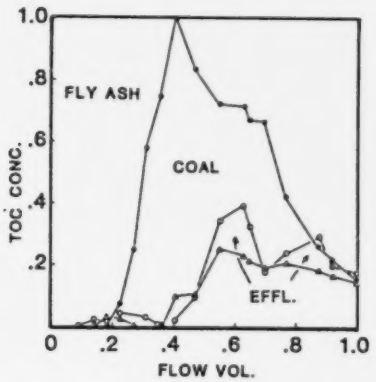


Figure 6. Breakthrough Curves for Columns 3 and 4, Runs 1 and 2

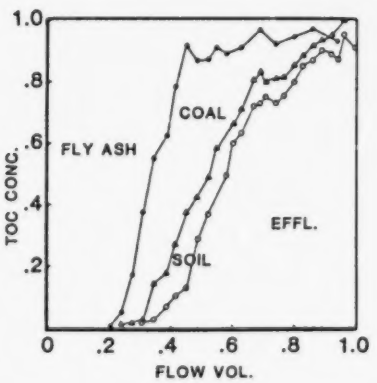
RUN #1
COLUMN 5



RUN #1
COLUMN 6



RUN #2
COLUMN 5



RUN #2
COLUMN 6

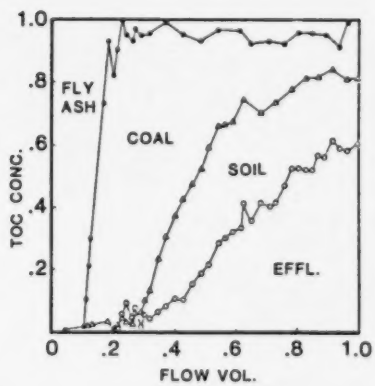
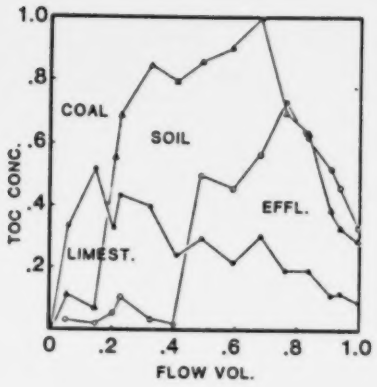
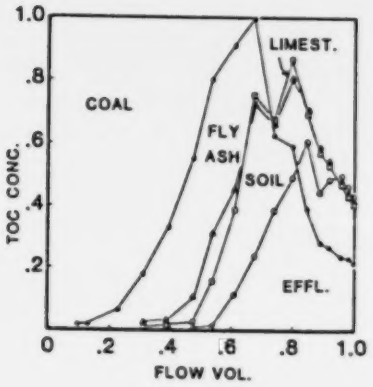


Figure 7. Breakthrough Curves for Columns 5 and 6, Runs 1 and 2

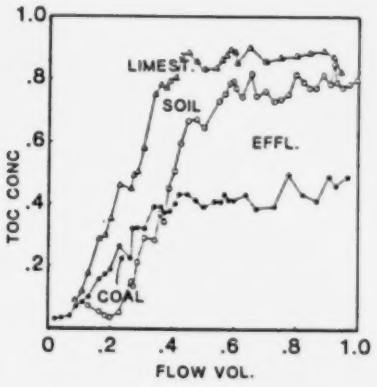
RUN #1
COLUMN 7



RUN #1
COLUMN 8



RUN #2
COLUMN 7



RUN #2
COLUMN 8

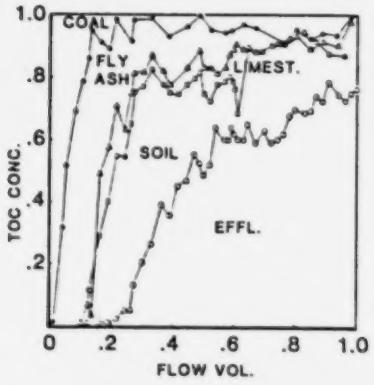
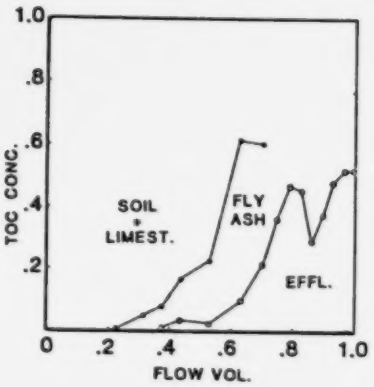
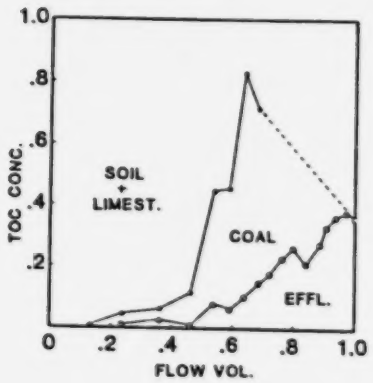


Figure 8. Breakthrough Curves for Columns 7 and 8, Runs 1 and 2

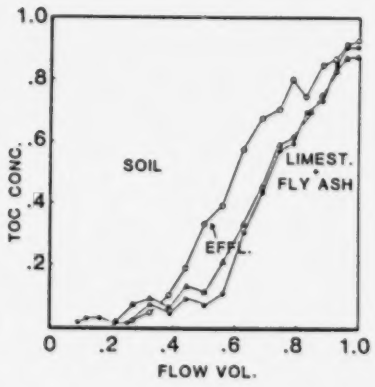
RUN #1
COLUMN 9



RUN #1
COLUMN 10



RUN #2
COLUMN 9



RUN #2
COLUMN 10

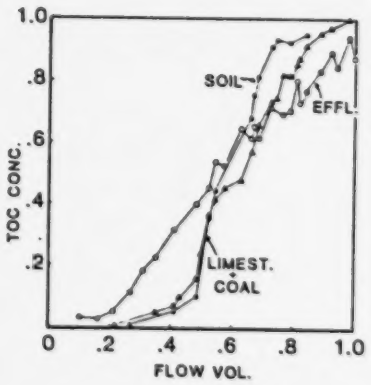
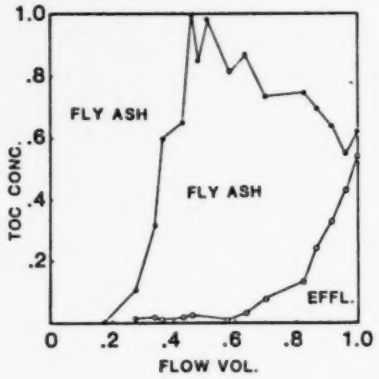
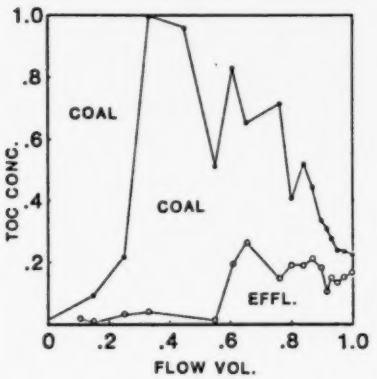


Figure 9. Breakthrough Curves for Columns 9 and 10, Runs 1 and 2

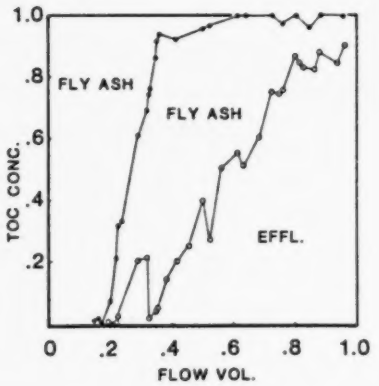
RUN #1
COLUMN 11



RUN #1
COLUMN 12



RUN #2
COLUMN 11



RUN #2
COLUMN 12

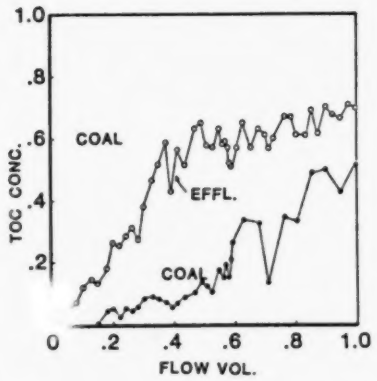


Figure 10. Breakthrough Curves for Columns 11 and 12, Runs 1 and 2

TABLE 4. RUN # 1 COLUMN PERFORMANCE

Column	Total Flow (L)	Total TOC Retained (mg)	Days to 50% Breakthrough	Linear Velocity (cm/day)	Permeability (cm/day)	Overall Ranking
1	7.18	6377	16	19.3	.78	8
2	6.66	7839	18	17.2	.73	6
3	6.79	5709	9	10.2	.96	11
4	3.93	5247	19	7.5	.41	10
5	8.95	7299	11	18.8	.98	4
6	7.74	6103	12	12.4	.85	9
7	6.47	5177	7	9.2	.91	12
8	9.22	10493	11	21.4	1.01	2
9	6.21	6567	12	27.8	.68	7
10	9.23	11683	18	23.5	.95	1
11	8.08	7900	19	9.4	.84	5
12	8.92	12274	7	22.2	.97	3

TABLE 5. RUN #2 COLUMN PERFORMANCE

Column	Total Flow (L)	Total TOC Retained (mg)	Days to 50% Breakthrough	Linear Velocity (cm/day)	Permeability (cm/day)	Overall Ranking
1	15.86	4448	26	34.5	.84	5
2	12.38	3857	39	21.7	.52	9
3	25.78	7064	30	13.8	1.12	3
4	11.86	4310	47	8.8	.50	8
5	23.99	6146	16	60.5	1.47	2
6	24.02	7525	37	41.2	1.01	1
7	26.12	6810	19	14.8	1.10	7
8	28.40	7006	20	16.0	1.19	4
9	14.35	3796	13	23.3	1.36	11
10	16.12	3911	14	25.9	1.00	12
11	17.00	4374	28	31.1	.77	6
12	29.44	6533	15	8.2	1.23	10

more likely to remain on the material if it were strongly sorbed. The elution results for coal indicate that adsorption may be an important part of its retentive capacity. It held up to 50% of the retained TOC following elution. The soil was able to hold up to 30% of its retained TOC in some samples but none in others. Thus, of the four materials tested only coal exhibited strong adsorptive capabilities.

BATCH TESTS

Along with the elution tests performed on the concentration-saturated materials, leaching tests using deionized water were performed on the unused materials in order to determine the background amounts of TOC that would elute from them. The results are found in Table 6. Also shown in Table 6 are the results of batch sorption tests using the Run #2 simulated hazardous waste leachate, two concentration of phenol, as well as the averages for the column results of the two runs. Especially noteworthy here is the lack of predictive value the batch sorption has with respect to the fly ash's and the soil's retentive capacities in the columns.

TABLE 6. BATCH TEST AND COLUMN AVERAGE TOC RESULTS

(All results are mg TOC/kg dry weight)

	Limestone	Fly Ash	Coal	Soil
Leaching with deionized H_2O (40 g in 100 ml)	4	20	26	14
Run #1 Retention Column Averages	0	286	813	552
Run #2 Retention Column Averages	32	323	498	348
Retention of Run #2 Feed 421 mg/l TOC (40 g in 300 ml)	0	92	624	57
Phenol 200 mg/l (120 g in 300 ml)	20	26	333	13
Phenol 100 mg/l (120 g in 300 ml)	7	17	174	3

RUN #1

ALL VALUES ARE MG/KG

L = LIMESTONE
C = COAL

F = FLY ASH
S = SOIL

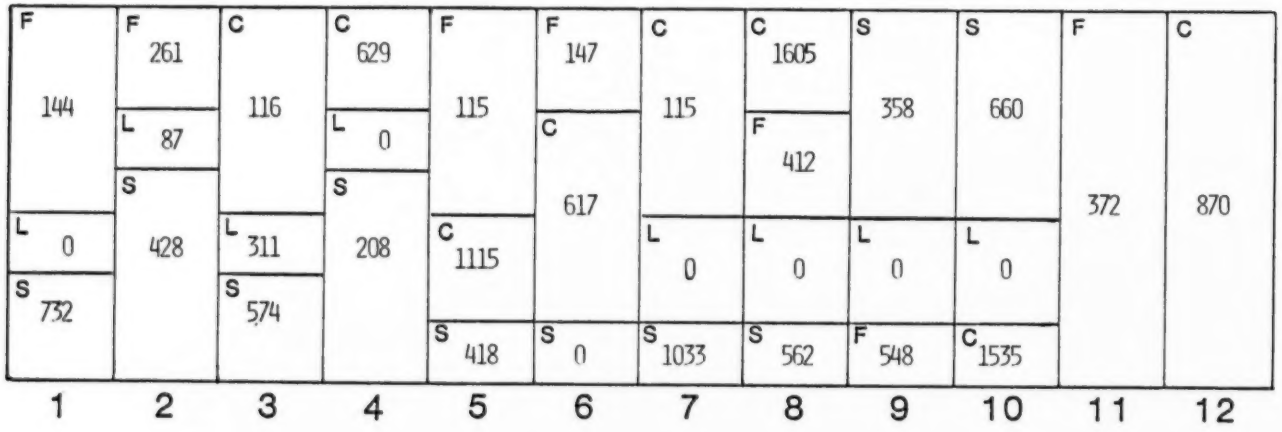


Figure 11. Run #1 Retention Results

RUN #2

ALL VALUES ARE MG/KG
( ) = ELUTION

L = LIMESTONE
C = COAL

F = FLY ASH
S = SOIL

1	2	3	4	5	6	7	8	9	10	11	12
F 293 (334)	F 319 (323)	C 776 (291)	C 467 (351)	F 360 (350)	F 373 (376)	C 535 (222)	C 364 (294)	S 345 (356)	S 339 (441)	F 215 (348)	C 463 (237)
	L 35 (309)		L 98 (287)		C 427 (459)		F 377 (421)				
L 33 (269)	S 172 (379)	L 0 (287)	S 177 (335)	C 452 (397)		L 0 (262)	L 66 (298)	L 0 (270)	L 21 (341)		
S 203 (363)		S 145 (341)		S 140 (399)	S 555 (362)	S 689 (403)	S 715 (390)	F 0 (427)	C 32 (544)		

Figure 12. Run #2 Retention And Elution Results

MOVEMENT OF PRIORITY POLLUTANTS

In addition to the determination of the retentive capacities of the materials with respect to TOC, twelve priority pollutants were examined as a part of the Run #2 simulated hazardous waste leachate. During the run, effluent samples from each column were composited over successive 5-day periods resulting in five samples for each, covering the first 25 days of the run. At the time of the last sample only columns 2, 4 and 6 had not reached an effluent TOC concentration of at least 150 mg/l. The results of the gas chromatographic analysis performed on these column effluent samples are presented in Table 7. The number in the second column of the Table reflects the total number of occurrences above the detection limits for any of the 12 compounds in any of the column's composite samples. Since there were 5 samples per column and 11 compounds, (phenanthrene and pentachlorophenol were indistinguishable) the total number of possible occurrences would be 55. The third column is the number of times any compound appeared at a concentration greater than 100 μg/l, which would indicate near-complete breakthrough. The compounds which were found at these concentrations are then listed. The numbers in parentheses indicate more than one occurrence greater than 100 mg/l. In nearly all cases though, when a compound was detected at a concentration greater than 100 μg/l in a sample, it was either not detected or at a much lower concentration in the subsequent sample. None of the compounds exhibited clear evidence of total saturation, even in the columns which were saturated according to the TOC breakthrough data. This would indicate that none of the 12 priority pollutants moved through the columns faster than the other organics measured as TOC.

The five compounds that did not appear in the effluents at concentrations above 20 μg/l were dichlorophenol, phenathrene, pentachlorophenol, fluoranthene, and pyrene. These proved to have only limited mobility regardless of the order of contact with the permeable material layers.

Bis(2-ethylhexyl) phthalate was measured in many of the samples at concentration greater than 250 μg/l despite a feed concentration of only 163 μg/l. This could have resulted from interference caused by the high concentration of potassium hydrogen phthalate in the feed or as a result of leaching from the plexiglas walls of the experimental apparatus.

Phenol appeared at high concentrations in some early samples, but then was not found in subsequent samples. It is possible that it leached from the coal or fly ash and was not retained by the permeable materials in the layers below. In the first samples, the effluent TOC concentrations ranged from 9-36 mg/l, with as much as 60 mg/l TOC leaching from the coal-only column. Batch tests using deionized water as previously discussed showed slight elution of organics, of which phenol would be a likely candidate.

The seven compounds that exhibited mobility comparable to that of the measured TOC then were: Bis(2-ethylhexyl) phthalate, Di-N-Butyl phthalate, dichlorobenzene, ethylbenzene, isophorone, phenol and naphthalene.

TABLE 7. RUN #2 PRIORITY POLLUTANT G.C. ANALYSES

Column	Total Occurences	Occurences >100 µg/L	Compounds >100 µg/L
1	30	2	Dibutylphthalate, Phenol
2	25	1	Phenol
3	21	1	Bis(2-ethylhexyl) Phthalate
4	13	1	Phenol
5	17	1	Bis(2-ethylhexyl) Phthalate
6	16	3	Phenol (2), Bis(2-ethylhexyl) Phthalate
7	20	5	Phenol (2), 1, 2 Dichlorobenzene, Bis(2ethyl...) Dibutylphthalate
8	10	0	
9	21	5	Bis(2-ehtylhexyl) Phthalate (2), Phenol, Isophorone, Dibutylphthalate
10	14	3	Napthalene, Dibutylphthalate, Ethylbenzene
11	14	4	Bis(2-ethyl...), Dibutylphthalate (2), Ethylbenzene
12	13	3	Bis(2-ethyl...), Dibutylphthalate (2)

( ) Indicates more than one occurrence.

Overall Column Performance and Orderings of Materials

An important aspect of this project was to determine the most appropriate ordering or orderings of the chosen permeable materials; that combination of materials that best retained the organic contaminants yet allowed a consistant, uniform flow of liquid. The criteria used for evaluating column performance and thus determining the most appropriate orderings reflected these concerns. Four criteria were chosen, two related to retention and two related to flow. The best performing columns then would exhibit good retention while permitting the largest volume of flow. The retention-related criteria were: 1) the number of days to 50% breakthrough and 2) the total TOC retained. The flow-related criteria were: 3) the linear flow velocity and 4) the calculated permeability coefficient. These values are listed in Tables 4 and 5.

The overall rankings for column performance were determined by assigning numerical values (1 through 12) to each of the columns for each of the four criteria. For example, in Run #1, column 12 retained the most TOC so it was given a "1" ranking while column 7 retained the least and received a "12". The four ranked criteria were totaled and the columns were ranked again, the lowest total receiving a "1". The original rankings were also multiplied together and these products were also reranked. The additive and multiplicative rankings were then added. The overall rankings were then taken from these results. These rankings are indicative of the responses of the columns to the simulated hazardous waste leachates used in the two runs.

Two problems with the materials can be discussed in terms of the overall rankings. In columns 2 and 4, the 20 cm layers of soil proved to hinder flow in both runs. This would not be a positive result for that material, so despite having long times to 50% breakthrough these two columns received low rankings. The other problem was channeling through the top coal layers, especially seen during Run #1 in columns 3 and 7. These columns likewise received low rankings.

Considering the results of Run #2, the two highest ranked columns were 5 and 6, both with a layer of fly ash above a coal layer. The next ranked column was number 3 which did not exhibit channeling as in Run #1. Column 8, also ranked high and additionally had the fewest occurrences of priority pollutants in its effluent. The rankings for Run #2 as well as the retention results indicate that the most appropriate ordering of the permeable materials tested would be a fly ash layer, followed by a coal layer, followed by a limestone layer. The fly ash would moderate the flow and reduce channeling, while the coal would be the primary retentive material. The limestone would raise the pH of the liquid that passed through the coal, precipitating cations. This was observed in all the limestone layers located below coal or fly ash layers. Rust-colored precipitate which was the iron leached from the coal or fly ash was visible between the limestone particles.

SECTION 6

CONCEPTUAL DESIGN EXAMPLES

The final objective of this project was to develop conceptual designs for applying the permeable materials to a field site. Three such conceptual designs were developed for remedial action activities. The site utilized for these exercises is a National Priority List (NPL) site in the Pacific Northwest which has been characterized both geologically and hydrologically and for which a reasonable amount of background environmental data was available.

The first conceptual design example is a down-gradient permeable treatment barrier intended to retain all pollutants. The second and third examples make use of a down-gradient collection system. The second example incorporates the ability to flush contaminants from the permeable material, while the third example is a modular, replaceable permeable treatment system.

ASSUMPTIONS

The groundwater flow at the site is predominately horizontal. The water table averages 2 m below the site surface. The first 3.7 m of soil is mainly fill of lower permeability than the underlying strata. These factors would indicate that contamination is predominately found in the upper 5 m of the soil. Since the bedrock is some 90 m from the surface, and a permeable barrier of this depth is unreasonable, not likely to be cost effective, so all designs will be based on a depth of 5 m below the surface, approximately 3 m below the water table.

The permeability at the site ranges from 10^{-2} to 10^{-5} cm/sec. Laboratory results indicate a permeability of 4.0×10^{-4} cm/sec.

Using the Darcy Equation: $Q = KiA$

where : Q = flow through the site ($L/Day/m^2$)
K = permeability (cm/sec)
i = hydraulic gradient
A = crossectional area (m^2)

and assuming that $i = 0.1$ and $A = 1\ m^2$ ($10{,}000\ cm^2$), then

$$Q = (4.0 \times 10^{-4}\ cm/sec)(.1)(10{,}000\ cm^2) = .4\ cm^3/sec = 34.5\ L/Day/m^2$$

This value will be used for all calculations.

The site has a maximum point concentration of trichloroethylene of 210 mg/l. There would undobtedly be more organic contaminants at lower concentrations. The estimated value for the groundwater organic contamination is 40 mg/l TOC, which would be considered high, averaged over the entire site. Because the inorganics may be treated by precipitation, the conceptual designs are based only on the treatment of organics.

The materials to be used in the design examples are assumed to be similar to those tested as a part of this project. The fly ash has a retentive capacity of 300 mg/kg, which was the same for both concentrations tested, while the coal's retentive capacity is assumed to be 400 mg/kg, lower than the test results because of the lower assumed contaminant level of 40 mg/l.

In order to intercept the groundwater flow from the site it would be necessary to run along both the north and west boundaries. The total boundary length is assumed to be 500 m.

Conceptual Design 1: Boundary Treatment Barrier

The goal of this design is to intercept the contaminated groundwater from the site with a vertical wall of permeable materials for a given length of time. Two years was chosen based on the large groundwater flow and the likelihood of rapid flushing of organics.

The primary design calculation is that of the thickness of the permeable barrier. Since the design is for the treatment of organics, and coal was determined in the laboratory tests to retain the most organics (as TOC), the assumption will be that the coal portion of the barrier must retain the full organic load for 2 years. The other materials then will serve to provide a margin of safety.

The TOC load per day/m^2 can be found by multiplying the flow times the concentration:

34.5 L/day/m^2 (flow per day) x 40 mg/l (average TOC conc.) =
1380 mg TOC/Day/m^2

Coal's retentive capacity = 400 mg TOC per Kg coal

Dividing the load by the retentive capacity:

$$= \frac{1380 \text{ mg TOC/day/m}^2}{400 \text{ mg TOC/kg coal}} = 3.45 \text{ kg coal used per day}$$

Coal's density in a barrier would be about 900 kg/m^3 or 9.0 kg per linear cm in a cubic meter block.

Dividing the daily coal usage per m^2 by the linear density:

$$\frac{3.45 \text{ kg coal/day}}{9.0 \text{ kg/cm}} = .38 \text{ cm/day}$$

This is the amount of coal completely used in retention each day. Over two years then, 2.8 m of coal would be required (730 days x .0038 m).

Figure 13 shows a plan view of the site with the location of the boundary treatment barrier. A cross sectional schematic shows the design dimensions chosen. Allowing a margin of safety, 3.0 m of coal would be used. The fly ash serves to moderate the flow as well as provide additional retention. The limestone will increase the pH of the groundwater as it passes from the coal. The thicknesses of the fly ash and limestone are proportional to the layers that were tested in the bench-scale project and proved useful.

The materials will be filled to a 5.0 m depth with approximately 2.0 m of freeboard to allow for rises in the water table and still provide treatment. Calculations based on in-place densities indicate the weights of the three materials needed would be: coal, 6.7×10^6 kg; limestone, 5.5×10^6 kg; and fly ash, 3.9×10^6 kg. It would be advisable to cover the barrier with an impermeable layer to prevent infiltration.

Conceptual Design 2: Flushable Barrier

It was found in the bench-scale project that the fly ash tested elutes all the organics retained when flushed with .01N $CaSO_4$. The flushable barrier design will make use of this property to concentrate the organics on the fly ash and then flush them off for suitable treatment. Following flushing, the fly ash will remain in place and be reused.

In order to efficiently treat the contaminated groundwater, French drains 5 m in depth will be used to route the flow to two treatment trenches. Figure 14 shows the location of these trenches. An impermeable plastic liner should be placed on the downstream side of the drain to prevent movement of contaminants off site and insure movement toward the treatment trenches.

The total flow from the site into the drain system may be calculated by:

500 m (drain length x 3 m (height of ground water in drain) = 1500 m^2, the total crossectional area

$$1500 \text{ m}^2 \times 34.5 \text{ L/day/m}^2 = 51{,}750 \text{ L/day (total flow)}$$

The TOC loading then is:

$$51{,}750 \text{ L/day} \times 40 \text{ mg/l TOC} = 2{,}070{,}000 \text{ mg TOC/day}$$

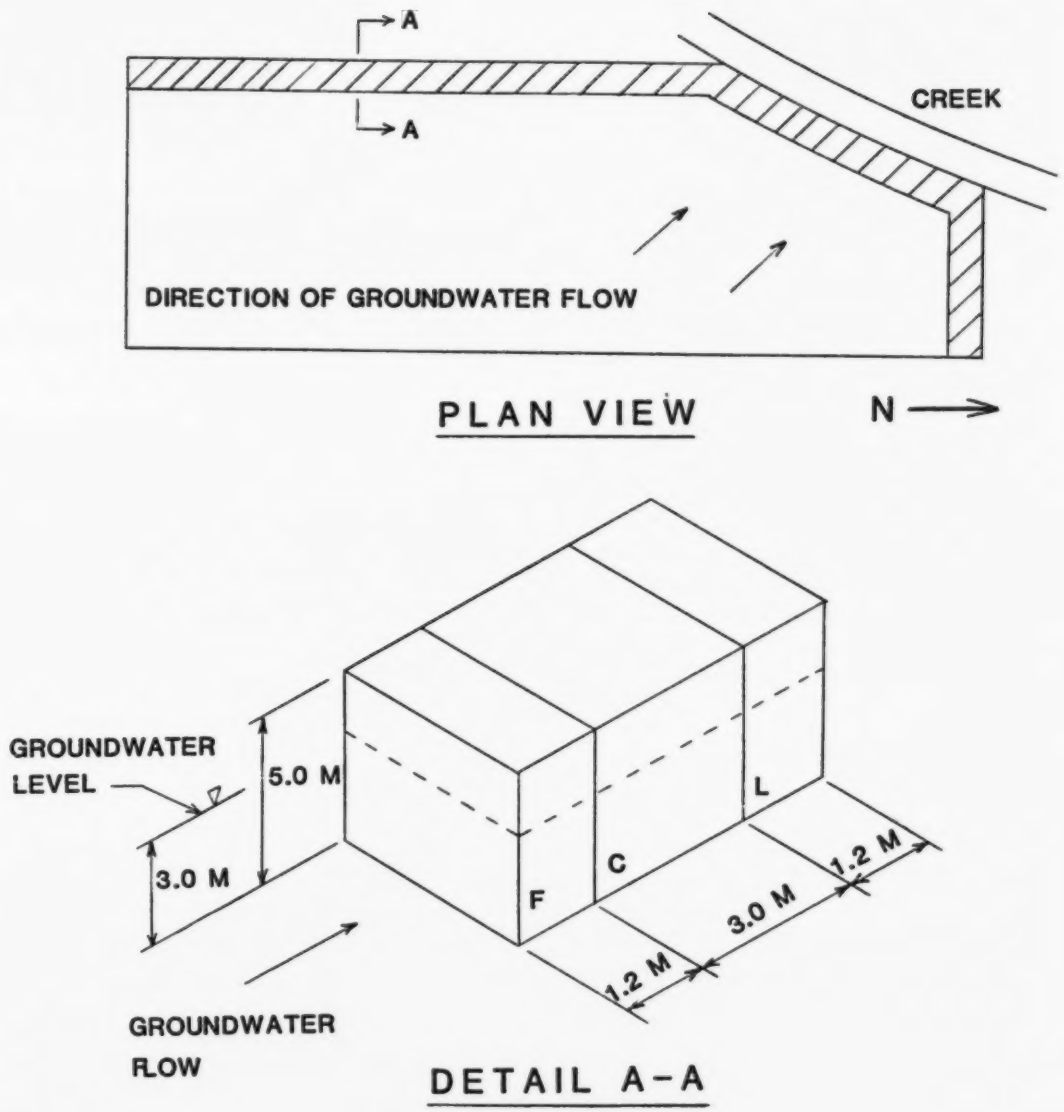


Figure 13. Conceptual Design 1: Boundary Barrier

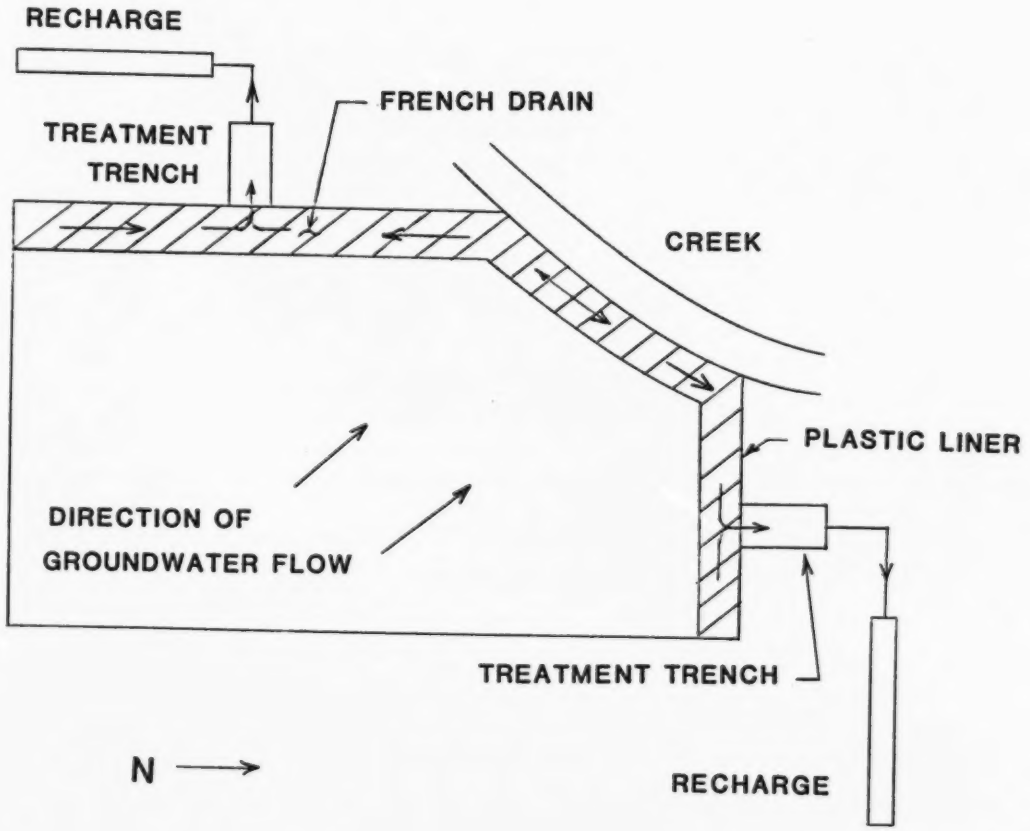


Figure 14. Conceptual Design 2 & 3: Collection System

Laboratory results show that fly ash retains 300 mg TOC/kg (dry weight). Assuming two treatment trenches and dividing the retention into half the TOC load:

$$\frac{1{,}035{,}000 \text{ mg TOC/day}}{300 \text{ mg/kg}} = 3450 \text{ kg fly ash used/day}$$

If each treatment trench is 10 m wide by 5 m deep (3 m below the water table), then the cross sectional area is 50 m^2. Fly ash's in-place density is 1300 kg/m^3 or 13 kg per cm of length per m^2. Thus each cm of length in a trench of 50 m^2 cross section with 30 m^2 below the water table contains 390 kg of fly ash per cm in contact with the ground water.

The amount of fly ash used per day can then be calculated by:

$$\frac{3450 \text{ kg/day (usage rate)}}{390 \text{ kg/cm (density)}} = 8.8 \text{ cm/day}$$

If each treatment trench were to be flushed every 6 months, then:

$$8.8 \text{ cm/day} \times 180 \text{ days} = 15.8 \text{ m}$$

or about 16 m in length. A schematic of the treatment trench is shown in Figure 15.

The sections of limestone will serve to precipitate cations and adjust pH as well as provide access for the drain and collection lines needed for flushing. The effluent pumped from the far limestone section will be piped to recharge basins located a suitable distance from the barrier drain. The recharge will be designed to maintain a hydrologic balance at the site.

Based on in-place densities for fly ash and limestone as 1300 kg/m^3 and 1850 kg/m^3 respectively, the calculated total weights for two treatment trenches would be 2.1×10^6 kg fly ash and 1.8×10^6 kg limestone.

Conceptual Design 3: Modular Treatment System

It may be desirable at a site to remove the spent permeable materials and properly dispose of them. This conceptual design addresses this possiblity. As in the previous example, a boundary collection drain, as shown in Figure 14 will be used to route the contaminated groundater to two treatment trenches.

The rationale behind this design is to use the most appropriate orderings of the permeable materials in modular, series-operated systems that can be replaced. As in the first example, coal will be the primary retaining material. The system is designed as if coal retains all the organic contaminants. The fly ash serves to moderate the flow and reduce channeling into the coal. It also serves as a safety factor providing additional retention of pollutants. The limestone adjusts pH following leachate contact with the coal.

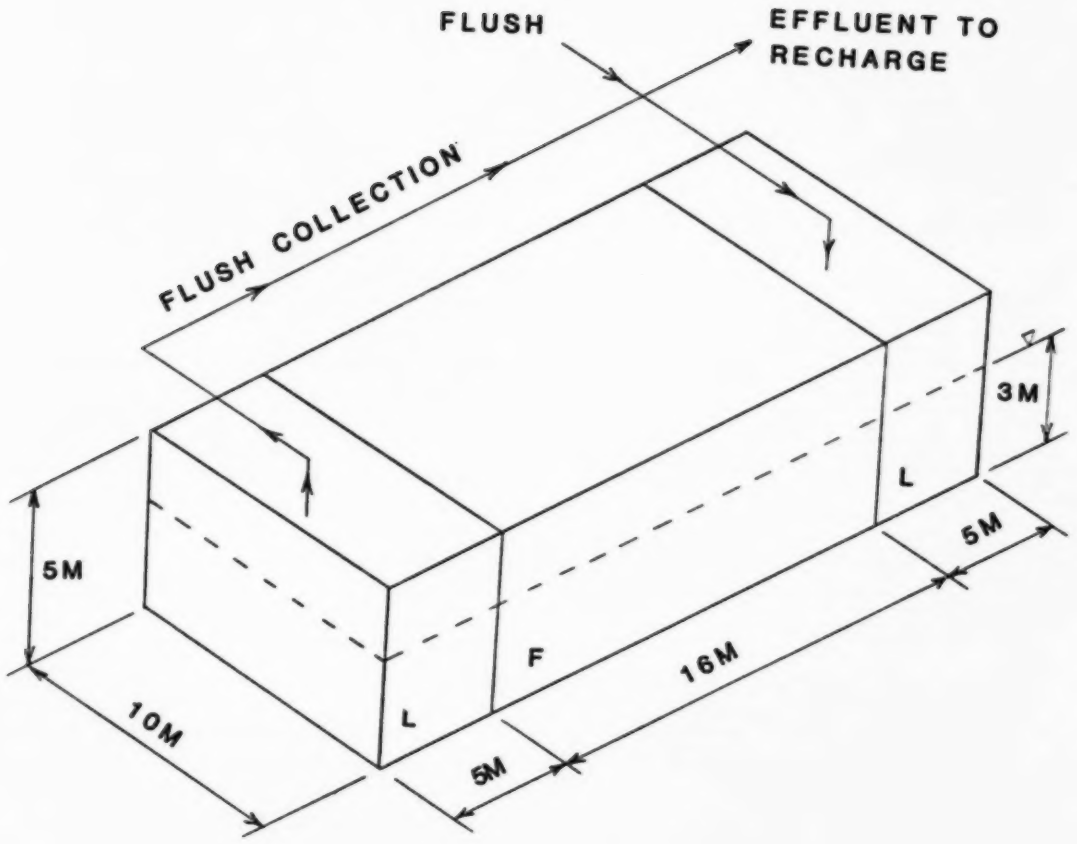


Figure 15. Flushable Treatment Trench

Using the infomation from the two previous designs, there would be a TOC load of 1,035,000 mg TOC for each of the two treatment trenches. If the same trench dimensions are used (from conceptual design 2) then there would be a 10 m x 5 m trench with 3 m below the water table. Dividing the TOC load by coal's retentive capacity [450 mg/kg (dry weight)], the amount of coal used per day is:

$$\frac{1{,}035{,}000 \text{ mg TOC/day}}{400 \text{ mg/kg coal}} = 2587 \text{ kg coal per day}$$

Coal's linear density per cm is 9.0 kg/cm/m^2. Using again a 30 m^2 cross section below the water table, the trench contains 270 kg of coal per cm length. The linear amount of coal used per day can be calculated by:

$$\frac{2587 \text{ kg coal/day}}{270 \text{ kg/cm}} = 9.6 \text{ cm/day}$$

If each section of the modular system for a trench is designed for a 6 month life, then:

$$9.6 \text{ cm/day} \times 180 \text{ days} = 17.3 \text{ m}$$

As shown in Figure 16, each coal section would be 17.5 m in length, allowing a margin of safety. The fly ash and limestone sections are in approximate proportions, as indicated by the laboratory results.

Drain lines and effluent collection lines will be located in the limestone sections. When the first module has completed its life, the flow will be collected in the first limestone section and pumped to the second module. The first module will then be excavated and replaced with fresh material.

Based on previously related in-place densities, the weights of the three materials used in two treatment trenches, each with 2 sections can be calculated. The weights required are: coal, 3.2×10^6 kg; fly ash, 7.8×10^5 kg; and limestone, 2.2×10^6 kg.

Assuming even distribution of contamination, over the same period of time, similar amounts of retaining material will be required for either Design 1 or Design 3, the differences between costs would be seen when construction is considered. Design 3 offers more control over the contamination by centralizing the system, making monitoring much easier.

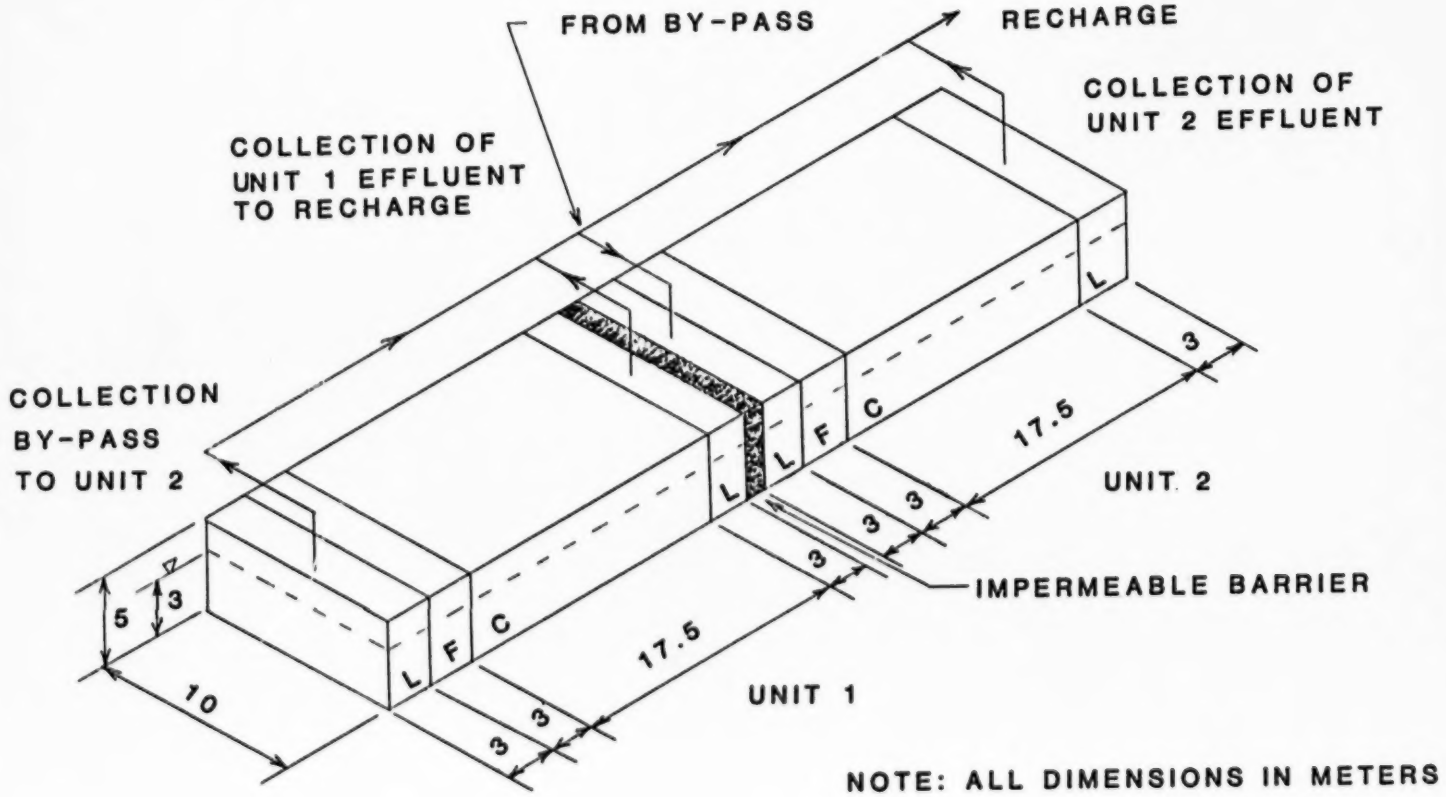


Figure 16. Modular Treatment Trench

REFERENCES

Alesii, B.A. and W.H. Fuller, "The Mobility of Three Cyanide Forms in Soils." EPA 600/9-76-015, pp. 213-223, 1976.

Artiole, J. and W.H. Fuller, "Effect of Crushed Limestone Barriers on Cr Attenuation in Soils." J. Envir. Qual. V.8, No. 4, 503-509. 1979.

Artiole, J. and W.H. Fuller, "Limestone Liner for Landfill Leachates Containing Be, Cd, Ni, and Zn." Soil Sci. 129 (3): 167-179, 1980.

Boynton, The Chemistry and Technology of Lime and Limestone, Wiley/InterSci. 2nd Ed., 1980.

Chan, P.C., R. Dresnack, J.W. Liskowitz, A. Perna, R. Trattner, "Sorbents for Flurice, Metal Finishing, and Petroleum Sludge Leachate Contaminant Control." EPA 600/2-78-024, 1978.

Chan, P.C., J.W. Liskowitz, A. Perna, R. Trattner, "Evaluation of Sorbents for Industrial Sludge Leachate Treatment." EPA 600/2-80-052, 1980.

Chou, S-F.J., R.A. Griffin, M.M. Chou, "Effect of Soluble Salts and Caustic Soda on Solubility and Adsorption of C-56." EPA 600/9-82-002, pp. 137-149, 1982.

Chou, S-F.J., B.W. Fisher, R.A. Griffin, "Aqueous Chemistry of Hexachlorocyclopentadiene by Earth Materials." EPA 600/9-81-002b, pp. 29-42, 1981.

Davidson, J.M., L-T. Ou, P.C.S. Rau, "Behavior of High Pesticide Concentration in Soil Water Systems." EPA 600/9-76-015, pp. 206-212, 1976.

Davidson, J.M., P.C.S. Rau, L-T. Ou, "Movement and Biological Degradation of Large Concentrations of Selected Pesticides in Soils." EPA 600/9-80010, pp. 93-107, 1980.

Dobbs, R.A. and J.M. Cohen, "Carbon Adsorption Isotherms for Toxic Organics." EPA 600/8-80-023, 1980.

Dragun, J. and C.S. Helling, "Soil and Clay-Catalyzed Reactions: I.; Physicochemical and Structural Relationships of Organic Chemicals Undergoing Free-Radical Oxidation." EPA 600/9-82-002, pp. 106-121, 1982.

Dragun, J. and C.S. Helling, "Evaluation of Molecular Modeling Techniques to Estimate the Mobility of Organic Chemicals in Soils: II.; Water Sollubility and Molecular Fragment Mobility Coefficient." EPA 600/9-81002b, 1981.

Elseewi, A.A., A.L. Page, S.R. Grimm, "Chemical Characterization of Fly Ash Aqueous Systems." J. Envir. Qual. V.9, No. 3, pp. 424-427, 1980.

Farquhar, G.J., "Leachate Treatment by Soil Methods." EPA 600/9-77-026, pp. 187-207, 1977.

Fuller, W.H., "Liners of Natural Porous Materials to Minimize Pollutant Migration." EPA 600/2-81-122, 1981.

Fuller, W.H., A. Amoozegar-Fard, E.E. Niebla, M. Boyle, "Influence of Leachate Quality on Soil Attenuation of Metals." EPA 600/9-80-010, pp. 108-117 (1980).

Fuller, W.H., A. Amoozegar-Fard, G.E. Carter, "Predicting Movement of Selected Metals in Soils: Applications to Disposal Problems." EPA 600/979-023a, pp. 358-374 (1979).

Fuller, W.H., N.E. Korte, E.E. Niebla, B.A. Alesii, "Contribution of the Soil to the Migration of Certain Common Trace Elements." Soil Sci. 122 (4), pp. 223-235 (1976a).

Fuller, W.H., C. McCarthy, B.A. Alesii, E.E. Niebla, "Liners for Disposal Sites to Retard Migration of Pollutants." EPA 600/9-76-015, pp. 112-126 (1976b).

Griffin, R.A. and S.J. Chou, "Disposal and Removal of Halogenated Hydrocarbons in Soils." EPA 600/9-80-010, pp. 82-92, 1980.

Griffin, R.A., R.R. Frost, A.K. Au, G.D. Robinson, N.F. Shimp, "Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals: Part II, Heavy Metal Adsorption." Envir. Geol. Notes, No. 79, 1977.

Griffin, R.A., K. Cartwright, N.F. Shimp, J.D. Steele, R.R. Ruch, W.A. White, G.M. Hughes, R.H. Gilkeson, "Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals: Part I, Column Leaching and Field Verification." Envir. Geol. Notes, No. 78 (1976a).

Griffin, R.A., R.R. Frost, N.F. Shimp, "The Effect of pH on the Removal of Heavy Metals from Leachates by Clay Minerals." EPA 600/9-76-015, pp. 259268 (1976b).

Griffin, R.A., N.F. Shimp, J.D. Steele, R.R. Ruch, W.A. White, G.M. Hughes, "Attenuation of Pollutants in Municipal Landfill Leachate by Passage Through Clay." ES&T, V.10, No. 13, pp. 1262-1268 (1976c).

Grim, R.E., Clay Minerology, 2nd Ed., McGraw Hill, 1968.

Humenic, M.J., L.N. Britton, C.F. Mattox, "Natural Restoration of Groundwater in UCG." InSitu 6(2), pp. 107-125, 1982.

Korte, N.E., W.H. Fuller, E.E. Niebla, J.K. Skopp, B.A. Alesii, "Trace Element Migration in Soils: Description of Attenuated Ions and Effects of Solution Flux." EPA 600/9-76-015, pp. 243-258 (1976).

Korte, N.E., J.K. Skopp, W.H. Fuller, E.E. Niebla, B.A. Alesii, "Trace Element Movement in Soils: Influence of Soil Physical and Chemical Properties." Soil Sci. 121(6), pp. 350-359 (1976a).

Korte, N.E., J.K. Skopp, E.E. Niebla, W.H. Fuller, "A Baseline Study on Trace Metal Elution from Diverse Soil Types." Water, Air, Soil Poll. 5: pp. 149156, 1975.

Malone, P.G. and R.A. Karn, "Toxic Metal Removal from Electroplating Wastewater Using Silyated Silica Gel." U.S. Army Eng. Waterways Exper. Sta., Sept. 1982.

Park, J.E., "The Sorption of Lead, Cadmium, Arsenic and Selenium By Coal." M.S. Thesis, CEE Dept., Univ. of Cincinnati, March 1983.

Roy, W.R., R.G. Thiery, R.M. Schuller, J.J. Suloway, "Coal Fly Ash: A Review of the Literature and Proposed Classification System, with Emphasis on Environmental Impacts." Envir. Geol. Notes, No. 96, 1981.

Sheih, M.S., "The Use of Natural Sorbents for the Treatment of Industrial Sludge Leachate." Dissertation, New Jersey Inst. of Tech., 1979.

Spoljaric, N., W.A. Crawford, "Removal of Metals from Laboratory Solutions and Landfill Leachate by Greensand Filters." Univ. of Delaware, Delaware Geol. Survey, Rept. of Invest. No 32 (1979a).

Spoljaric, N., W.A. Crawford, Removal of Contaminants From Landfill Leachates by Filtration Through Glauconated Greensands." Envir. Geol., V.2, No. 6, pp. 359-363 (1979b).

Theis, T.L. and R.O. Richter, "Chemical Speciation of Heavy Metals In Power Plant Ash Pond Leachate." ES&T 13(2), pp. 219-224, 1979.

Theis, T.L. and J.C. Wirth, "Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems." ES&T 11(12), pp. 1096-1100, 1977.

Walters, E.A. and T.M. Niemczyk, "The Effects of Underground Coal Gasification on Groundwater." Draft Document, IERL, EPA, 1982.

Wang, F., "The Sorptive Properties of Coal." LLNL Preprint, DOE, 1980.